Study of the Process & Mechanism of Plating Directly on Titanium and Its Alloys

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A new process has been developed for forming an active film on the surface of titanium and its alloys, which can then be electroplated, much like nickel, copper or chromium. The technology can assure the adhesion of the electroplated coating. In addition, the paper discusses the mechanism of the "active film" formation.

Titanium and its alloys have many excellent properties, such as light weight, high strength, good corrosion resistance, and high-temperature resistance. They have been widely used, therefore, in various industrial applications. Titanium alloys are most promising in aerospace applications. Nevertheless, titanium has its surface defects, such as poor wear resistance, large contact resistance, low electric conductivity, and poor weldability. As a result, these defects have restricted development of further applications, causing research into the surface treatment of titanium and its alloys to become very important.

Electroplating, as one of the effective surface treatment technologies, can not only ameliorate the above-mentioned defects of titanium and its alloys, but endow their surfaces with new special physical properties as well, so as to satisfy the requirements for practical applications. The main difficulty in plating on titanium is the poor binding strength of its plated coating. Because the activity of titanium is very great, it will be oxidized quickly in a medium containing oxygen; a compact oxide film will be formed on its surface that has very high chemical stability. It is this oxide film that hinders close binding between the basis metal and the applied coating. To date, no plated coating with a great enough binding strength has been obtained. The conventional procedure for plating on titanium is as follows:[1,2]

Blasting —> degreasing —> etching —> activating —> dip plating or electrolytic preplating —> plating —> heat treatment

Although the procedure is complicated, it hardly ensures that the plated coating will have satisfactory adhesion.

The key to attainment of the satisfactory adhesion is elimination of the surface oxide film and retention of the activity of the titanium surface. Practically, the real difficulty of the study lies in the latter, the reason being that when a titanium workpiece is taken out of the acid etching bath, unavoidably it will contact the air and water before being plated. As a result, a passivating film will be quickly reformed on its surface. Through experiments, the authors have found an appropriate activating solution and its corresponding activating process that will be able to cause the generation of a dark gray film, called "active film," on the titanium surface. When plating is performed immediately on such a film, a satisfactory layer will be obtained.[3]

The XPS, XRD methods, etc., were used to determine the composition and structure of the film; its formation and mechanism of action were explored further.

Experimental Procedure

Materials

Industrial-purity titanium specimen (TA_2) or titanium alloy specimen $Ti_6Al_4V(TC_4)$, 1.5 mm in thickness.

Procedure

TA_2 or TC_4 specimen —> degreasing —> etching —> activation —> plating.

Etching[4]

Etching for 5 min at room temperature.

Etching solution:	Nitric acid (65%)	80 mL/L
	Hydrofluoric acid (42%)	60 mL/L
	Hydrogen peroxide (30%)	150 mL/L

Activation of Titanium (TA_2)

Activating treatment for 20 min at room temperature. A uniform dark gray color is formed.

Activating solution:	Hydrochloric acid (37%)	500 mL/L
	Titanium trichloride (15-20%)	15 mL/L
	Surfactant	2 g/L

Activation of Titanium Alloy (TC_4)

Activating treatment for 10-15 min at room temperature until formation of a gray-black film.

Activating solution:	Amides	400-600 mL/L
	Hydrofluoric acid (40%)	100-150 mL/L
	Surfactant	2-3 g/L

Electroplating of Nickel on Titanium and its Alloys (TC_4)

After activation, titanium can be electroplated with nickel or chromium routinely.

Adhesion Tests

1. Bending method
   The specimen was placed in a bench clamp and bent into a right angle. The electroplated coating was checked for blisters, then bent into a straight angle.
2. Heating
   The specimen was placed in an oven at a temperature of 250 °C for an hour, then cooled in water at room temperature.
3. Alternating cold and hot treatments
   The specimens were tested in periodic cold and hot alternating treatments for 50 cycles. A typical cycle is: 110 °C —> room temp —> -195.8 °C (liquid nitrogen) —> room temp —> 110 °C.

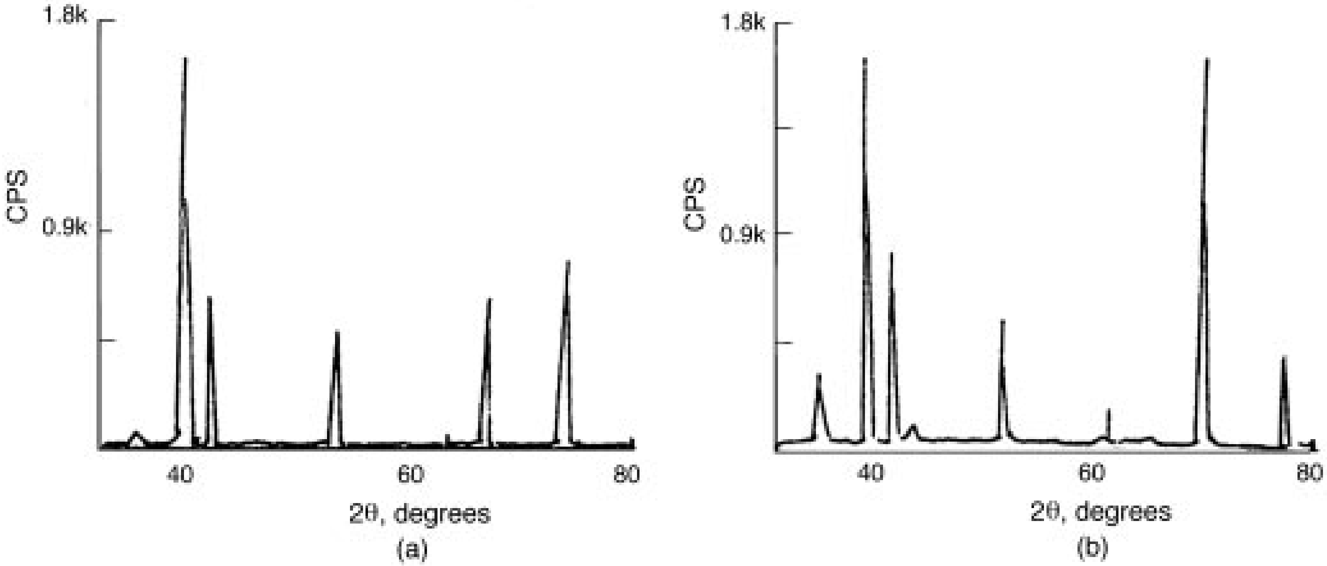

Fig. 1—XRD analysis of TA_2: (a) etched specimen; (b) activated specimen.

4. Drawing test

   A multi-electronic experimental machine was used to measure the adhesion of the electroplated coating. Experiments show that on the surface of titanium and alloys, the adhesive force of a nickel layer is above 337 kgf/cm^2.

Electro-potential Measurements

Electro-potential measurements were made during the activation process.

XRD Analysis

An automatic diffraction instrument was adopted to determine the composition and structure of the "active film" formed on the TA_2 specimen after activating treatment.

XPS Analysis

ESCA was adopted to analyze the elemental constituents of the samples and their valence states before and after activation treatment; then a deep analysis of the samples was made through Ar$^+$ ion etching.

Results and Discussion

Adhesive Force

The drawing experiments show that on the surface of the titanium and its alloys, the adhesion strength of the nickel coating is above 337 kgf/cm^2. Because of the limitation of the epoxy adhesive itself, its upper limit of adhesive force cannot be measured.

XRD and XPS Analysis

Appearance of the sample

After etching, the appearance of the sample was bright. After activating treatment, a grayish-black compact film was formed that had excellent binding strength with its base metal.

XRD analysis

The result of XRD analysis is shown in Fig. 1. When the two diffraction spectrograms are compared, it can be seen that there are several more diffraction peaks for the activated sample than for the inactivated sample. It can also be seen that some diffraction peaks appear comparatively weak, as a

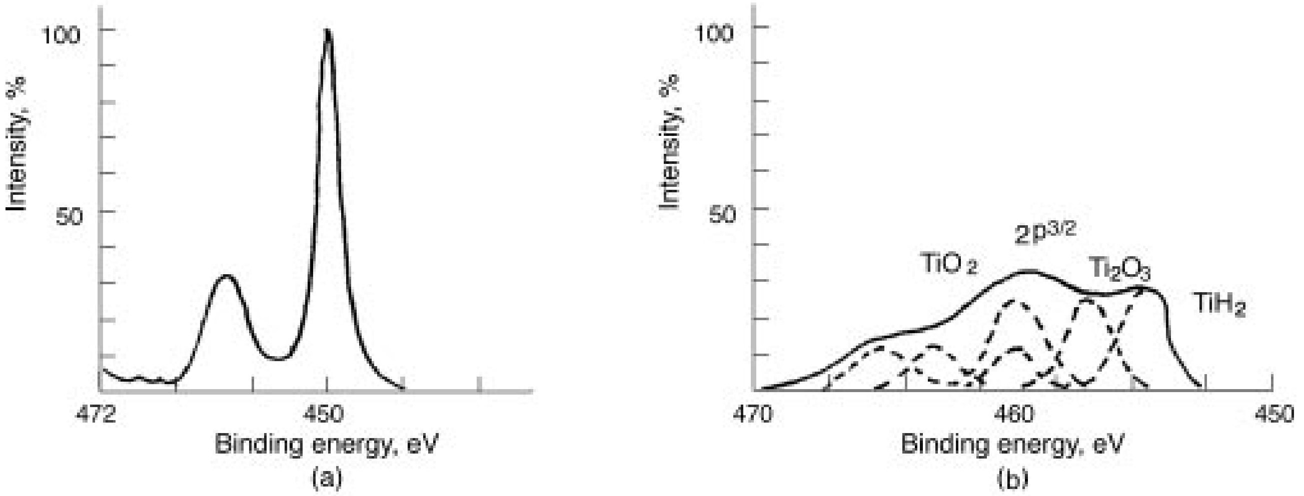

Fig. 2—XPS analysis of TA_2: (a) etched specimen; (b) activated specimen.

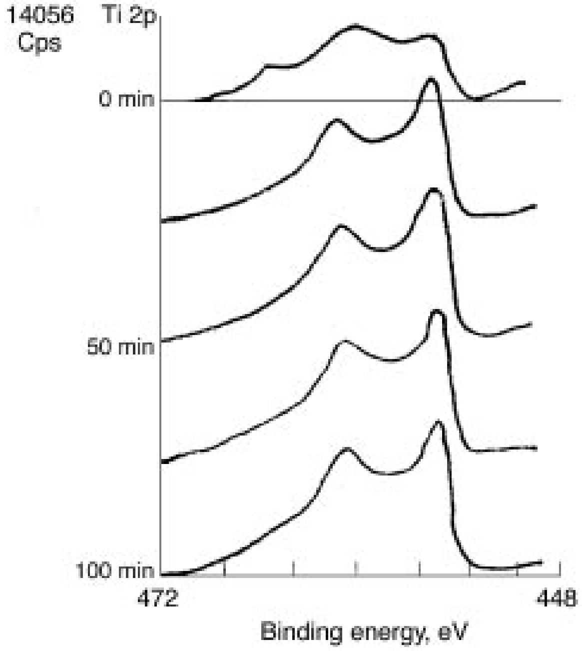

Fig. 3—ESCA analysis of activated TA_2 in depth.

result of the very thin "active film," but they are just the characterized diffraction peaks of TiH_2. This implies that the "active film" contains TiH_2.

XPS analysis
Figure 2 shows the binding energy (BE) spectrograms of the TA_2 sample. From Fig. 2a, it can be seen that the titanium BE of the two peaks are Ti $2P^{3/2}$: 459.8 eV; Ti $2P^{1/2}$: 465.1 eV. This corresponds to the titanium BE in TiO_2 (Ti $2P^{3/2}$: 495.1 eV and Ti $2P^{1/2}$: 464.8 eV). It follows that almost all the titanium exists in the form of TiO_2.

From Fig. 2b, it can be seen that titanium exists in many states after separating the diffraction peaks in the spectrogram; generally, Ti $2P^{3/2}$ exists in three states: 454.6 eV, 457.3 eV, and 459.3 eV. In contrast with the standard spectrogram, it can be seen that they are the Ti $2P^{3/2}$ electronic BE of TiH_2, Ti_2O_2 and TiO_2, respectively. It follows that the "active film" contains TiH_2 and oxides of titanium.

Existence of titanium oxides in the "active film" most probably results from oxidization of titanium in the air. A deep analysis of the specimen was made, therefore, through Ar^+ ion etching (see Fig. 3).

From the deep analysis of the "active film," it can be seen that after sputtering for 25 min, its BE (Ti $2P^{3/2}$) is about 454.6 eV, and no oxide of titanium exists in the specimen surface. Titanium exists only in the form of TiH_2, and its surface shows a dark gray color. This also proves that the previous deduction is true.

XPS analytical results
It is found by XPS that results for TC_4 are the same as for TA_2. Figure 4 shows the variation of electro-potential vs. activation time when the TA_2 sample is treated in the activating solution. It can be seen from Fig. 4 that at the beginning of the activating process, the electro-potential of the TA_2 specimen varies drastically; then, after about 30 min, it tends to stabilization; finally, its stability value reaches about -0. 556 V (b-c section).

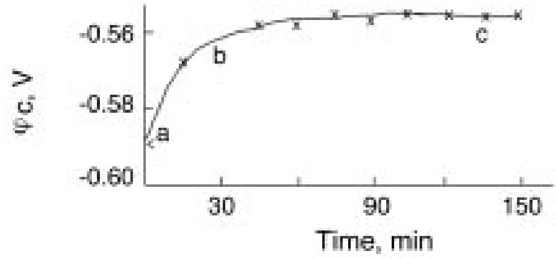

Fig. 4—φc vs. time during activation.

When the electro-potential of the TA_2 specimen varies drastically at the beginning of the activating process, the main reactions occur as follows:

Dissolution of the oxide film

$Ti_2O_3 + 6H^+ + 2e^- \langle—\rangle 2Ti_{+2} + 3H_2O$ φ °= -0.248 V

$TiO_2 + 4H^- + e^- \langle—\rangle Ti^{+3} + 2H_2O$ φ°= 0.029 V

The reaction is completed very quickly.

Dissolution of titanium

$Ti \langle—\rangle Ti^{+2} + 2e^-$ φ° = -1.63 V

$Ti^{+2} \langle—\rangle Ti^{+3} + e^-$ φ° = -0.368 V

Reduction of H^+ occurs at the same time.

Reduction of hydrogen ions

$H^+ + e^- \langle—\rangle [H]_{ad}$

Part of the $[H]_{ad}$ is compounded, resulting in deposition (inclusion) of H_2; the remainder of the $[H]_{ad}$ reacts with the active titanium, forming TiH_2.

Formation and dissolution of titanium hydride

$2[H]_{ad} + Ti \langle—\rangle TiH_2$

With the increase of TiH_2 formed on the surface of the TA_2, the potential tends to stabilize. In the b-c section, where the potential becomes stable, its titanium surface is completely covered by TiH_2. According to the ψ-pH diagram of the Ti-H_2O system, it can be understood that when the activation system is operating in the TiH_2 activation area, it implies that TiH_2 is being gradually dissolved.[5]

$TiH_2 \langle—\rangle Ti^{+2} + 2H^+ + 4e^-$ φ°= -0.59 V

At the same time, TiH_2 also reacts as follows:

$Ti + 2H^+ + 2e^- \langle—\rangle TiH^2$ φ°= +0.45 V

At the beginning of formation of the "active film," the speed of TiH_2 formation is faster than that of its dissolution, which makes the thickness of the film increase more and more until it is relatively balanced between film formation and film dissolution at the stage of stabilization.

Properties and Characteristics of the "Active Film"

Through observation and analysis, the titanium has a bright appearance after etching, and the main constituents of the surface film are oxides of titanium. This is because the active atoms of the etched titanium surface are exposed to the air. When the sample is treated in the activating process, its appearance turns to grayish black. The surface film is chiefly composed of the hydrides of titanium, but titanium oxides exist in the outer layers. The key to plating on titanium, therefore, is how to choose appropriate activating solutions and operating conditions so as to cause formation of a compact and relatively stable TiH_2 film on the surface. Its thickness should be appropriate; if too thick, it is apt to be considerably loose; otherwise, it is apt to be oxidized. Both of these results will have an effect on the binding strength of the coating. In addition, it is worthwhile to note that the "active film" should be exposed to the air as little as possible to avoid oxidation.

Action of the "Active Film"

When a titanium is activated, copper, nickel and chromium can be plated on it immediately with very satisfactory binding strength. The "active film"—TiH_2—plays an important role via the following two aspects.

Protective Action

Titanium is a very active metal. Its outer electronic configuration is $3d^2 4s^2$ and easily loses four outer electrons. Accordingly, titanium will be oxidized in air or water and quickly form a compact oxide, film (passivated film). As mentioned earlier, this is the reason that when plating directly on titanium, it is difficult to obtain satisfactory binding strength.

Our study of TiH_2 indicates that in the chemical bonds formed between Ti and H, there exists ion bond compounds, and that the electronic clouds have a bias toward H that makes them bear a negative electric charge. This decreases the density of outer electronic clouds in titanium, or, in other words, decreases the reaction activity of titanium, which makes titanium difficult to be oxidized quickly and to form a compact "passivated film."

Binding Action

Our study also indicates that TiH_2 has the properties of a metal, and that its outer electrons are free electrons, possessing the off-normal property. Because in TiH_2 the 3d orbit of titanium is half-full, many 3d orbits of TiH_2 are superposed to form an energy band. The energy of this band is similar to that of the base metal Ti and 2d band, and they will be superposed to form a metal band; meanwhile, this band will also be superposed with that of the coating metal to form a metal band. The "active film"—TiH_2—then binds itself to the base metal by such metal bonds and produces a coating with satisfactory binding strength.

Conclusions

Titanium and its alloys can be plated successfully with adherent deposits of nickel or chromium. The key to plating directly on titanium is to obtain a coating with satisfactory binding strength. Our study indicates that the chemical activation method will make titanium form a compact "active film" on its surface. The film consists mainly of TiH_2, and can not only reduce the chemical activity of titanium and avoid passivating its surface, but also possess the property of metal bonds and bind itself closely with the base metal in the form of metal bonds. In this way, a coating with satisfactory binding strength has been obtained and the key problem has been solved successfully.

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